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Electrical Properties of Al-Doped CdO Thin Films Prepared by Thermal Evaporation in Vacuum

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Abstract

In this work, thin films of undoped and Al-doped CdO with 3, 5, 7 and 9 wt.% were prepared by thermal evaporation in vacuum on glass substrate. From XRD patterns, doping CdO films with Al up to 7 % causes small reduction in the intensity of the (200) plane, while small increase is observed in the intensity of (111) plane. However, intensity of all peaks rapidly decreases for the films with high Al content (9 %). The formation of tubular nanostructures of undoped and Al doped-CdO films was observed by SEM technique. Energy gap value of the films was evaluated from the optical transmission spectra in the spectral region 300-1000 nm. The best values of electrical conductivity, Hall mobility and electron concentration were obtained in the films with 5% Al doping. Temperature dependent resistivity measurements of the films doped with Al at 3, 5 and 7 % showed the metal-semiconductor transition around 100, 150 and 205 K respectively, which is rationalised by localisation of degenerate electrons in a weak-localisation regime. It was also found that the transition temperature is dependent on the Al concentration and is related to the increase in disorder induced by dopant addition.

Keywords: CdO thin films; electrical properties; metal-semiconductor transition

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1. Introduction

Pure and metal doped degenerate semiconductor cadmium oxide (CdO) has been used in a wide range of optoelectronic application like transparent conducting oxide (TCO), solar cells, smart window and optical communication. The type and properties of doped ions control the electrical and optical properties of CdO films. It was found that some metallic ions like Sn, In, Sc, Al and Y of smaller radius than that of Cd^{2+}(0.097 nm) when doped in CdO films improve its electrical conduction and increase its optical band gap [1]. Some rare-earth ions like Eu, Dy, Sm, etc. could also be used as dopant in order to improve the CdO electrical conduction [2]. For mentioned cases, doped CdO has an n-type degenerate semiconducting properties. Different methods have been adopted to deposit these films such as sol-gel, dc magnetron sputtering, rf sputtering, spray pyrolysis, pulsed laser deposition, chemical vapour deposition and chemical bath deposition. Among them, there are few works reported in the literature with respected to Al doped-CdO films obtained by thermal evaporation method [3, 4]. In this work, we have prepared Al-doped CdO films by thermal evaporation technique. The effects of Al doping on the structural, electrical and optical properties of Al-doped CdO films were investigated.

2. Experimental details

Al-doped CdO films have been deposited on glass substrate by thermal evaporation in vacuum better than $5x10^{-5}$ mbar without heating the substrate. The glass substrates were cleaned with detergent, degreased with acetone, ethanol and rinsed with deionised water in an ultrasonic cleaner and finally etched in a 10% HF solution. Precursor for thermal evaporation were prepared by taking appropriate amount of commercially available polycrystalline CdO powder and different amounts of $Al(NO_3)_3$ H_2O so that Al atomic percentages in the mixture were 0, 3, 5, 7 and 9 %. The powders were mixed in a mortar thoroughly for 1 h and it was then pressed into pellet form by hydrostatic pressure about 6 GPa. The pellets contained with different Al percentages were heated in air at 800 °C for 24 h. The obtained films were then annealed in air at 200 ºC for 24 h. The crystal structure of these films was checked by X-ray diffraction technique with a Brucker D8 diffractometer using CuK_α radiation. Optical transmission measurements were performed with UV/Vis Jasco 7800 spectrophotometer. The band gap (E_g) of the transparent films determined from the optical transmission spectra. Ohmic contact was made of silver paste on the surface of CdO films. Electrical resistivity and Hall effect were measured in the van der Pauw configuration at room temperature. The type of the conducting carriers was determined to be n-type for all samples from the observed negative slope in magnetic field vs. Hall voltage plots. Carriers concentration and carrier mobility were calculated using the Hall coefficient and the resistivity data. The cryogenic system with a He closed cycle allows us to measure electrical resistivity of the films from 20 to 300 K by using a cryostat model RDK10-320 supplied by Leybold vacuum.

3. Results and discussion

The XRD patterns of the films are showed in Fig. 1. The existence of multiple diffraction peaks of (111), (200), (220), (311) and (222) planes indicates the polycrystalline nature of the CdO compound with cubic NaCl structure. Doping CdO films with Al up to 7 % causes small reduction in the intensity of the (200) plane, while small increase is observed in the intensity of (111) plane. However, intensity of all peaks rapidly decreases and full width at half maximum (FWHM) increases for the films with high Al content (9 %). This behaviour can be associated with the presence of Al-Cd compounds in the amorphous phase and with a diminishing of the CdO grain size. The lattice parameter decreases from 4.698 to 4.669 Å when Al percentage increases from 0 to 9 %. Typical SEM image of undoped and CdO films doped with 5 % Al was shown in Fig. 2. The formation of tubular nanostructures with length around 1 μm and diameter of 100-150 nm were observed on undoped CdO films. Smaller diameter and small length were observed in CdO films doped with 5 % Al. It can also be seen that some of the nanotubes appear straight in morphology, while many of them were usually twisted with several straight parts.

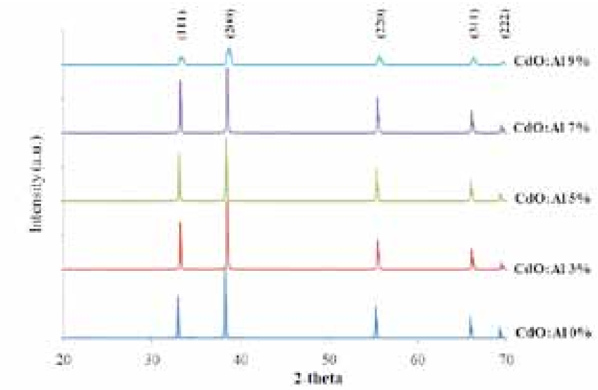
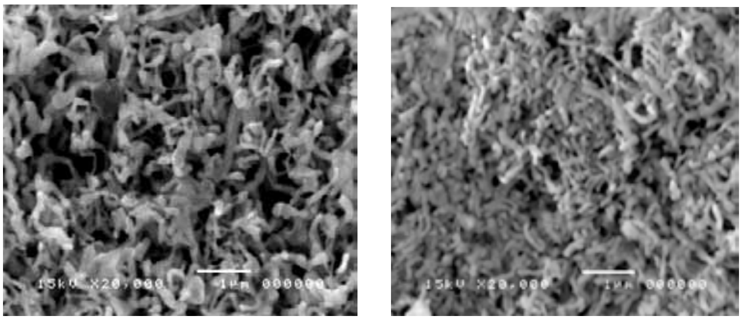


Fig. 1. XRD patterns of $Cd_{1-x}Al_xO$ films.



(x = 0) (x = 0.05)

Fig. 2. SEM image of $Cd_{1-x}Al_xO$ films for (a) x = 0 and (b) x = 0.05.

The carrier concentration n is derived from the relation $n = 1/(eR_H)$ where R_H is the Hall coefficient and e is the absolute value of the electron charge. The carrier mobility μ is determined using the relation $1/(ne\rho)$ where ρ is the resistivity. From Fig. 3, it is seen that the electrical resistivity of the films first decreases with Al content, attains a minimum at 5 % Al, and then increases with an increase in Al content. Whereas, the carrier concentration first increases with increase in Al contents and then decreases. The mobility initially increases with an increase in Al contents up to 5 % and then decreases with an increase in Al contents. These results indicate that the resistivity, carrier concentration and mobility of Al-doped CdO films are sensitive to the amount of Al doping. The increase in conductivity can be explained by the increase in carrier concentration due to Al addition. The values of resistivity, carrier concentration and Hall mobility for different Al doped CdO films are listed in Table 1. From Fig. 4, it can be seen that a minimum in resistivity is observed at low temperature for samples containing 3, 5 and 7 % Al, respectively. The temperature corresponding to a minimum in resistivity is called metal-semiconductor transition temperature [5, 6]. The transition temperature shifts to higher temperature for films doped with higher Al content: from 100, 150 to 205 K for the films doped with 3, 5 and 7 %, respectively. This indicates that the films doped with higher Al contents prefer semiconducting nature for longer temperature range. The negative temperature coefficient of resistivity (TCR) below the transition temperature and positive TCR above the transition temperature suggests that more than two competing mechanisms are operative [6]. The negative TCR observed below the transition temperature indicates localisation of electrons and the positive TCR above the transition temperature shows delocalisation. This delocalisation of electrons leads to metallic conductivity, which is characteristics of a degenerate semiconductor.

At temperature below transition temperature, if the electrons are localised due to a strong interaction, the conduction occurs by thermally activated motion which is known as the variable range hopping (VRH) mechanism. The conductivity in this case is given by the expression

$$\sigma = A\exp\left(-B/T^{1/4}\right) \tag{1}$$

where $B = 4E/\left(kT^{3/4}\right)$, E is the activation energy and A is a pre-exponential constant. The activation energy values calculated from the slope of Fig. 5 were listed in Table 2. These values are extremely small compared to kT, which suggest that the conduction does not occur by activated motion and electrons seem to be weakly localised. In the weakly localised regime, electrical conductivity is given by the expression [6]

$$\sigma = \sigma_B\left[1-\frac{C}{\left(k_F\ell\right)^2}\left(1-\frac{\ell}{L_i}\right)\right] \tag{2}$$

where σ_B is the Boltzmann conductivity, C is a constant of the order 1, l is the mean free path and L_i is the inelastic diffusion length equal to $(D\tau_i)^{1/2}$. Also, since $\tau_i \propto 1/T$, $L_i = \left(\hbar D/kT\right)^{1/2}$, which leads to $\sigma \propto T^{1/2}$. In a system with disorder, localisation occurs due to the constructive interference of scattered electrons, which decreases the conductivity. In the point of view Arrhenius law, activation energy value can be obtained from the relation $\rho = \rho_o\exp(E/kT)$ where ρ_0 corresponds to the resistivity value measured at 20 K. For the films with x = 0 and 0.09, the activation energy value was calculated from slope in Fig. 7. So, undoped and CdO films doped with 9 % Al display the characteristic of semiconductor behaviour.

From the transmittance spectra (in Fig. 8) we have also calculated optical band gap of films with different Al contents. The absorption coefficient α is calculated using the equation

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \tag{3}$$

where T is transmittance and d is film thickness. The absorption coefficient α and the incident photon energy hν related by the following equation [7]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{4}$$

where A and Eg are constant and optical band gap, respectively. The E_g can be determined by extrapolation of the linear portion of the curve to the photon energy axis. Figure 9 shows the curve of $(\alpha h\nu)^2$ vs. photon energy $(h\nu)$ of the films doped with 5 % Al. Band gap value is found to decrease with increase of Al doping contents (up to 5 %) and then start to increase again with higher Al doping content (Fig. 10). Generally one can expect an increase in band gap of CdO thin films when doped with Al due to an increase in carrier concentrations which lead to the Burstein-Moss effect. The increment of carrier concentrations of Al-doped films with respect to undoped films is not very large. In the undoped CdO films the carrier concentrations was already high, 2.93x10^{18} cm^{-3}. With Al doping it increased to maximum value of 1.64x10^{20} cm^{-3}. Hence, the increment of the band gap due to the Burstein-Moss shift is not large. Also there are other factors responsible for the changes of band gap, particularly for a degenerate semiconductor, electron-dopant interaction and electron-electron Coulomb and exchange interaction within the conduction band can lead to a shrinkage or renormalisation of the band gap of CdO as described by Dou *et al*. [8, 9]. The decrease in optical band gap for CdO films with different Al contents are consistent with previous report of Al-doped CdO films prepared by sol-gel [7] and of rf sputtering methods [9].

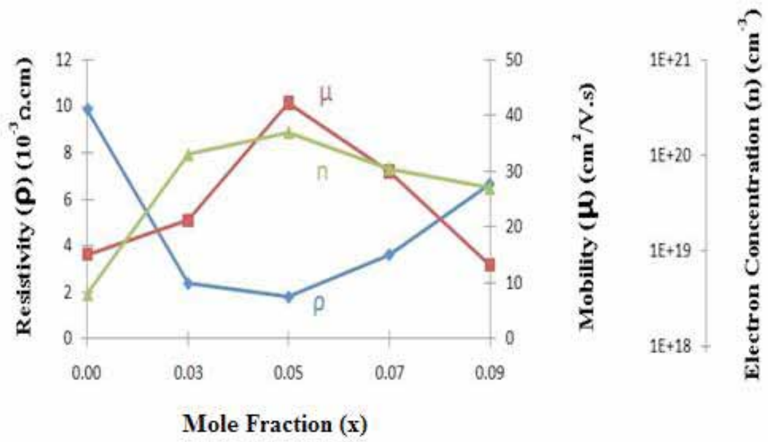


Fig. 3. Resistivity, Hall mobility and electron concentration for $Cd_{1-x}Al_xO$ films.

Table 1. List of values of resistivity, electron concentration and Hall mobility of $Cd_{1-x}Al_xO$ films

Mole fraction (x) of $Cd_{1-x}Al_xO$	Resistivity (10^{-3} Ωcm)	Hall coefficient (cm^3/C)	Electron concentration (cm^{-3})	Hall mobility ($cm^2V^{-1}s^{-1}$)
0	9.86	0.468	2.93x10^{18}	15.13
0.03	2.38	0.036	1.04x10^{20}	21.21
0.05	1.80	0.038	1.64x10^{20}	42.27
0.07	3.62	0.088	7.10x10^{19}	30.01
0.09	6.65	0.153	4.08x10^{19}	13.23

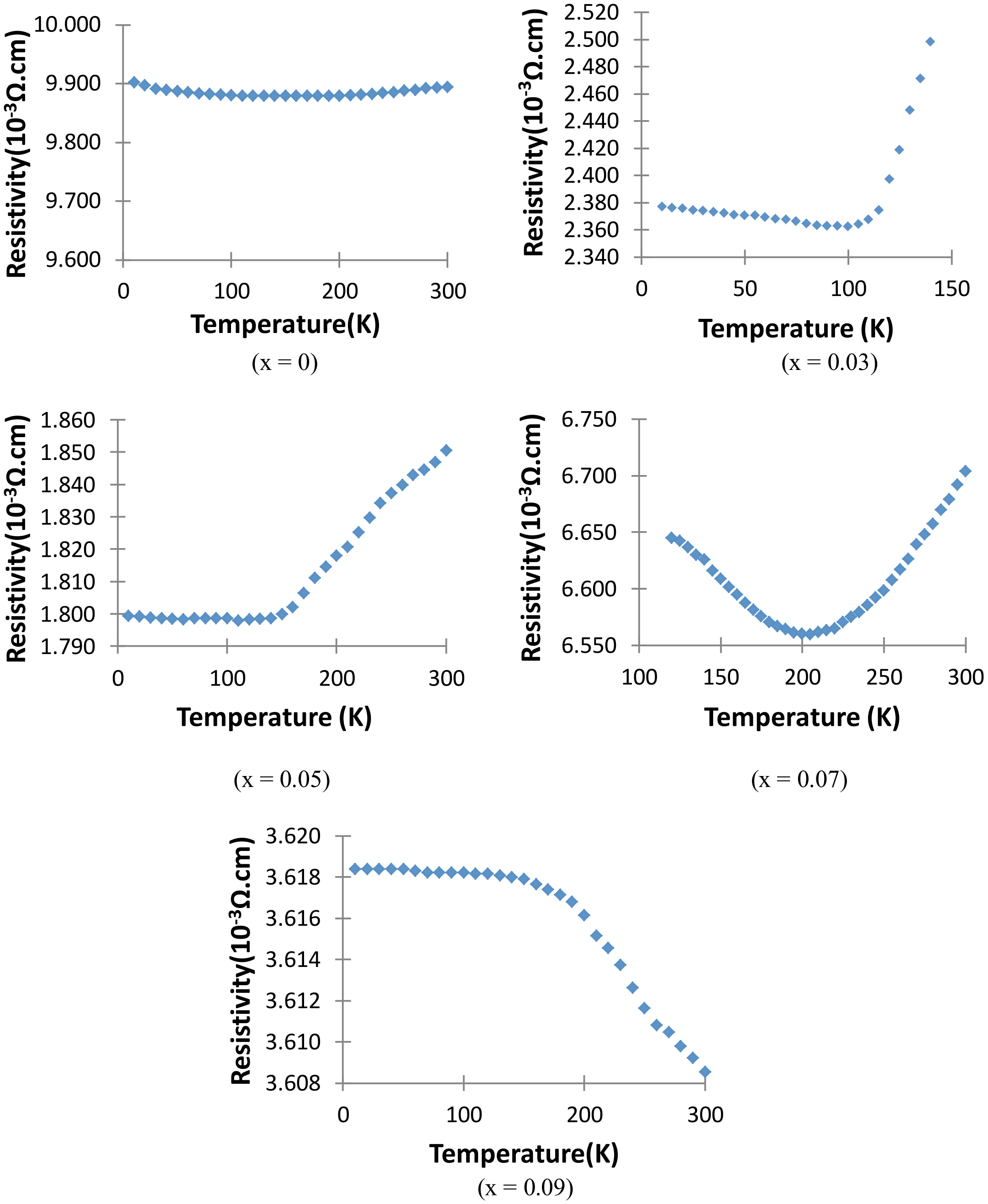
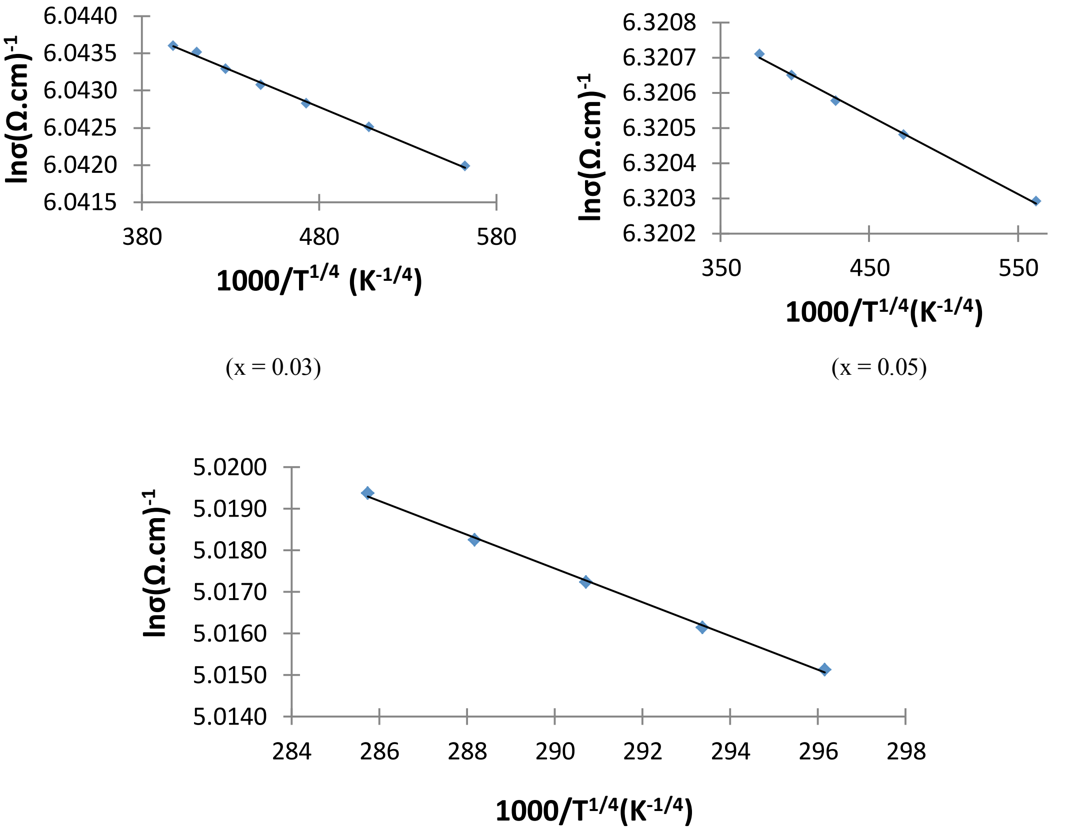


Fig. 4. Variation of resistivity as a function of temperature for $Cd_{1-x}Al_xO$ films.



(x = 0.03) (x = 0.05) (x = 0.07)

Fig. 5. Plot of ln σ vs $1000/T^{0.25}$ at temperature below the transition temperature for $Cd_{1-x}Al_xO$ films for x = 0.03, 0.05 and 0.07.

Table 2. List of values of metal-semiconductor transition temperature and activation energy of $Cd_{1-x}Al_xO$ films.

Mole fraction (x) of $Cd_{1-x}Al_xO$	Transition temperature (K)	Activation Energy (meV)	
		Degenerate semiconductor VRH (at T = 20 K)	Non-degenerate semiconductor
0	-	-	0.003
0.03	100	$2.04x10^{-3}$	-
0.05	110	$6.12x10^{-4}$	-
0.07	205	$8.16x10^{-2}$	-
0.09	-	-	0.13

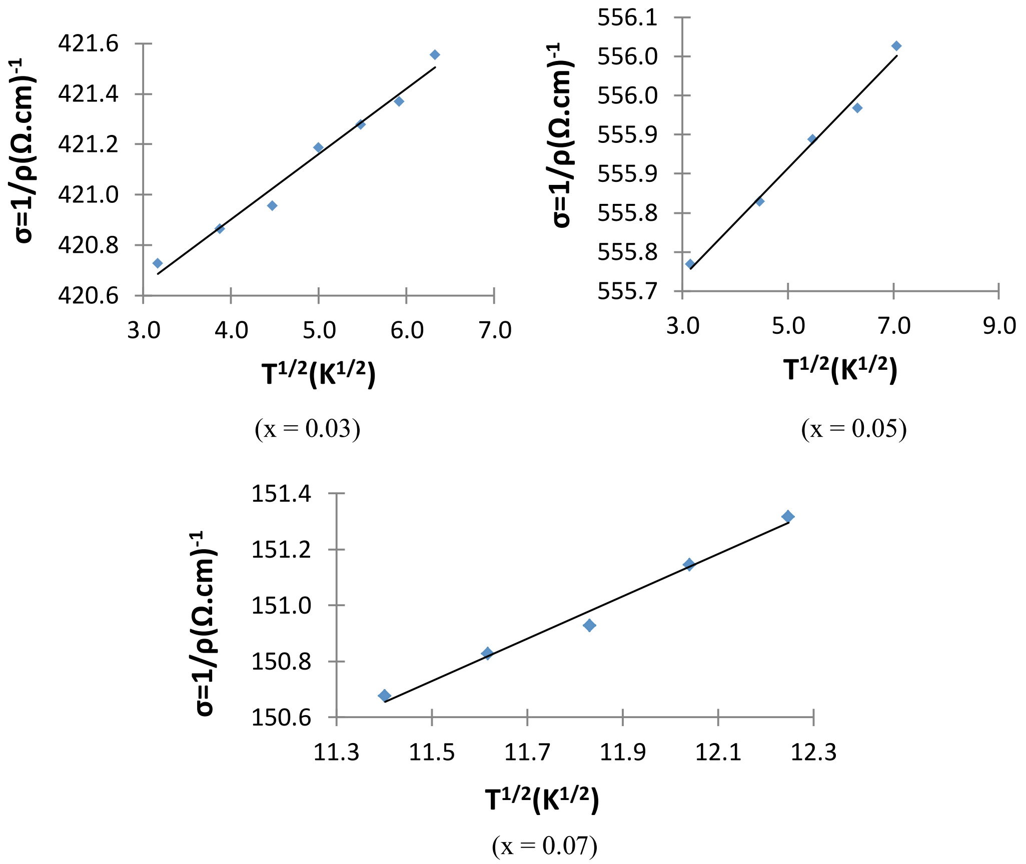


Fig. 6. Plot of σ vs $T^{1/2}$ at temperature below the transition temperature for $Cd_{1-x}Al_xO$ films for x = 0.03, 0.05 and 0.07.

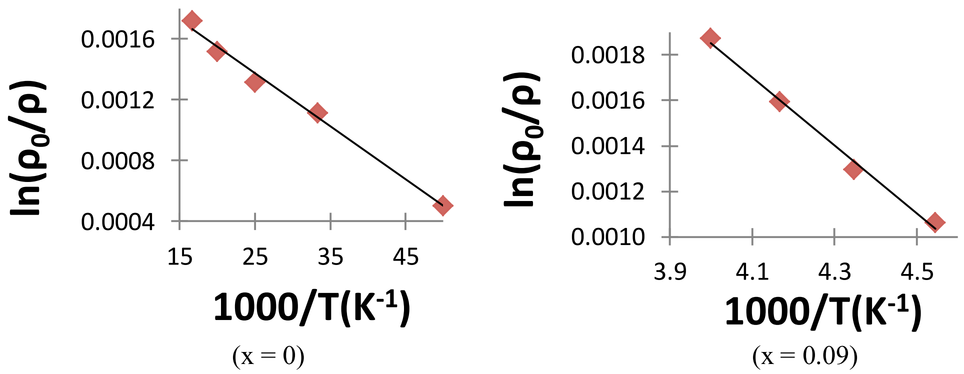


Fig. 7. Plot of $\ln(\rho_0/\rho)$ vs $1000/T$ for the $Cd_{1-x}Al_xO$ films for x = 0 and 0.09.

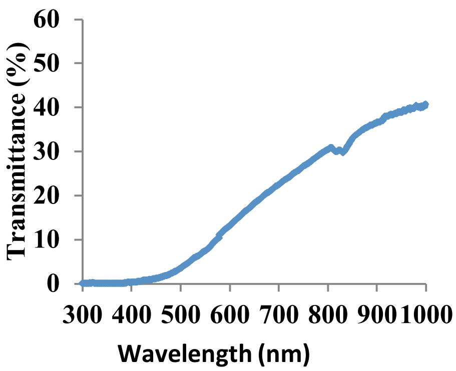


Fig. 8. Transmittance of $Cd_{1-x}Al_xO$ films for x = 0.05.

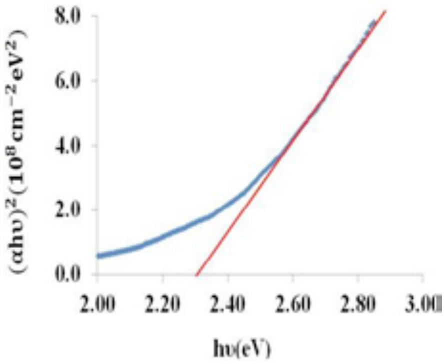


Fig. 9. Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for $Cd_{1-x}Al_xO$ films for x = 0.05

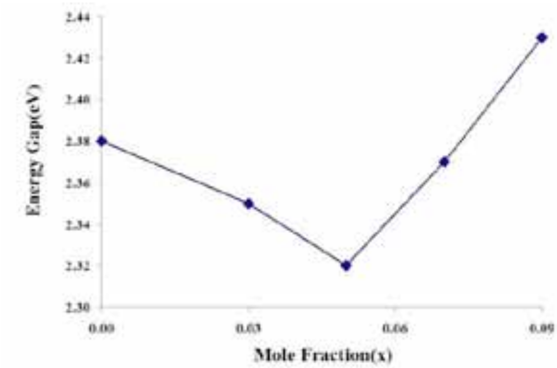


Fig. 10. Variation of energy gap of $Cd_{1-x}Al_xO$ films as a function of mole fraction *x*.

4. Conclusions

Undoped and Al-doped CdO films were deposited by thermal evaporation in vacuum on glass substrate without heating substrate. The effect of Al doping content on the optical and electrical properties was studied. It is observed that the electrical properties of the films depend on the Al content. The conductivity, carrier concentration and mobility of the films were measured at room temperature. The lowest resistivity (1.80×10^{-3} Ωcm) and high mobility (42.27 $cm^2V^{-1}s^{-1}$) is observed for the 5 % Al-doped CdO films. Transition from semiconductor to metallic behaviour occurs around 100, 150 and 205 K for 3, 5 and 7% Al-doped CdO films, respectively. Low resistivity, high mobility and wide band gap suggest that these films have significant commercial relevance.

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